A SIMPLE METHOD FOR PREDICTING SOOTING TENDENCIES OF HYDROCARBON FUELS IN PREMIXED FLAMES

Stamoulis Stournas and Euripides Lois

Chemical Engineering Department,National Technical University
42 Patission Street, 106 82 Athens, Greece

ABSTRACT

One of the accepted measures of sooting tendencies of hydrocarbon fuels in premixed flames is the threshold fuel/oxidizer ratio, φ_c,which assumes combustion to CO_2 and H_2O. In this analysis it has been found that this sooting can be accurately predicted by using the group additivity approach based on the nature of the individual carbon atoms that exist in the fuel molecule. The only parameters needed for this prediction are the numbers of sp^3, sp^2, sp, aromatic and benzylic carbons along with the total number of hydrogen atoms in the molecule.

This approach has been used for the calculation of the sooting tendencies of 73 fuels whose measured φ_c has been reported in the literature. Even though the structure of these fuels varied widely and included alkanes, olefins, alkynes and aromatics, the calculated values were always very close to the measured ones. In fact, in 88% of the cases the predicted values lie within 5% of the measured ones, whereas the deviation in the rest never exceeds 10%.

INTRODUCTION

The sooting tendencies of hydrocarbon fuels, either in premixed or diffusion flames, has been studied in the past by a number of investigators (1-12).

A number of parameters have been recognized as important aspects for the sooting tendency of a fuel, such as its molecular structure, fuel/oxygen ratio, flame temperature, etc.

Most of the recent work refers to efforts made to quantify these parameters into a unified approach that will predict the soot threshold of each fuel. More recently, Olson and Pickens (1) investigated a number of probable expressions defining soot thresholds for premixed flames for a large number of hydrocarbons, including alkanes, alkenes, alkynes and aromatics. A few years earlier, Haynes and Wagner (5) discussed soot thresholds for premixed flames, in a comprehensive review of soot formation in terms of critical C/O ratios, $(C/O)_c$.

Olson and Pickens assumed two modified equivalence ratios, one giving combustion products CO_2 and H_2O (φ_c), and the other CO and H_2O (ψ_c); the former was linked eventually with the Threshold Soot Index (TSI) as defined by Calcote and Manos (6).

In the present analysis, we have found that, by using the group additivity principle (13) the sooting tendency of hydrocarbon fuels can be predicted with good accuracy. Group additivity has been successfully used in the past to predict properties such as heat of formation, heat capacity, refractive index, etc.(14); more recently, it has been found useful in the prediction of ignition quality (cetane number) of diesel fuels.(15) Our approach was to divide the carbon atoms that comprise the fuel molecules into groups according

to their chemical nature (sp^3, sp^2, aromatic, etc.) and to assign a different weighting factor to each group. The only other information that is needed for the prediction is the total number of hydrogen atoms in the molecule.

ANALYTICAL APPROACH

Soot threshold is defined by the appearance of the first visible yellow emission as the fuel to air ratio was increased (1,16). This critical fuel to air ratio (F_c), when compared to the stoichiometric fuel to air ratio (F) that is required by the combustion process, gives a measure of the sooting tendency of each particular fuel.

If complete combustion to CO_2 and H_2O is taken as the basis of comparison, then the required stoichiometry for any hydrocarbon fuel C_nH_m is:

$$C_nH_m + \frac{4n+m}{4} O_2 \longrightarrow nCO_2 + \frac{m}{2} H_2O \qquad (1)$$

In this case the stoichiometric fuel/air ratio is given by

$$F = \frac{4}{4n+m} \quad \text{(moles fuel/moles oxygen)} \qquad (2)$$

and the sooting tendency depends on φ_c, defined as

$$\varphi_c = \frac{F}{F_c} = \frac{4}{(4n+m)F_c} \qquad (3)$$

On the other hand, by assuming combustion to CO and H_2O, the stoichiometry is:

$$C_nH_m + \frac{2n+m}{4} O_2 \longrightarrow nCO + \frac{m}{2} H_2O \qquad (4)$$

with

$$F = \frac{4}{2n+m} \quad \text{(moles fuel/moles oxygen)} \qquad (5)$$

The sooting tendency criterion is now ψ_c, defined as:

$$\psi_c = \frac{F}{F_c} = \frac{4}{(2n+m)F_c} \qquad (6)$$

It is clear that φ_c and ψ_c are related by the expression

$$\psi_c = \frac{(4n+m)\varphi_c}{2n+m} \qquad (7)$$

A third criterion, s_c, may be employed as a measure of sooting tendency, if we assume incomplete combustion to elemental carbon and water:

$$C_nH_m + \frac{m}{4} O_2 \longrightarrow nC + \frac{m}{2} H_2O \qquad (8)$$

In this case,

$$F = \frac{4}{m} \quad \text{(moles fuel/moles oxygen)} \qquad (9)$$

and the sooting tendency criterion, s_c, is defined as:

$$s_c = \frac{F}{F_c} = \frac{4}{mF_c} \qquad (10)$$

Also

$$s_c = \frac{(4n+m)\varphi_c}{m} \qquad (11)$$

This last expression permits the computation of the actual s_c for all fuels whose φ_c has been measured experimentally and whose gross structure (i.e. number of carbon and hydrogen atoms in the molecule) is known.

It is recognized that combustion to carbon and water is a rather unrealistic process; as will be shown later, however, s_c is a useful criterion for a unified approach to the prediction of sooting tendencies of hydrocarbon fuels and, by employing relations (7) and (11), it can lead to the better known quantities φ_c and ψ_c.

The relative amounts of carbon and hydrogen in a fuel molecule (in the form of hydrogen content) has been used as a rather intuitive guide to the sooting tendency of hydrocarbon fuels in both premixed and laminar flames, albeit with rather limited success. If, however, the effect of each carbon atom in the fuel molecule is accorded a weighting factor according to its chemical nature, an almost quantitative prediction of sooting tendency can result. We have found that it is sufficient to divide the various types of carbon atoms into five categories:

1. Saturated (sp^3) carbon atoms (C_1)
2. Olefinic (sp^2) carbon atoms (C_2)
3. Acetylenic (sp) carbon atoms (C_3)
4. Aromatic carbon atoms (C_A)
5. Benzylic carbon atoms, i.e. those directly coupled to an aromatic ring (C_B).

For the purpose of this definition, olefinic carbon atoms that belong to conjugated double bonds are counted as aromatic.

Based on the above definitions, the sooting tendency of any hydrocarbon fuel can be accurately predicted in the form of s_c by the relation:

$$s_c = \frac{3.5C_1 + 2.9C_2 + 1.9C_3 + 3.1C_A + 5C_B}{m} \qquad (12)$$

where C_1, C_2, etc. are the numbers of each type of carbon atoms as defined above, and m is the total number of hydrogen atoms in the molecule.

Alternatively, φ_c and ψ_c can be calculated for any fuel by changing the denominator in (12) with (4n+m) and (2n+m) respectively, where n is the total number of carbon atoms in the molecule.

RESULTS AND DISCUSSION

Relation (12) was applied to 73 hydrocarbon fuels whose sooting tendencies have been measured experimentally.(1,2,4,12) The calculated value of φ_c was within ±5% of the experimental value in 64 of the cases, and even in the worst case (1,5-cyclooctadiene) the difference was less than 10%. The linear correlation coefficient (r) between calculated φ_c and experimental φ_c for all the fuels was 0.95; this value can be considered as quite acceptable, given the wide variation in the molecular structure of the fuels (26 paraffins, 20 olefins, 7 alkynes, and 20 aromatics) and the inherent experimental uncertainties in measuring the critical fuel to air ratio. In several cases the values reported by different

investigators for the same fuel differ by more than 10%; the experimental values employed in this work were the averages of the reported values. The results of the calculations are depicted graphically in Figure 1, whereas Table I contains some examples that illustrate the calculation procedure.

Similar results were obtained in the calculation of ψ_c for the same fuels, except that the linear correlation coefficient was somewhat better (r=0.97).

TABLE I
EXAMPLES OF CALCULATED SOOTING TENDENCIES

FUEL	FORMULA	C_1	C_2	C_3	C_A	C_B	EXPERIMENTAL φ_c	EXPERIMENTAL s_c	CALCULATED φ_c	CALCULATED s_c
Propane	C_3H_8	3	0	0	0	0	0.524	1.309	0.525	1.313
iso-Octane	C_8H_{18}	8	0	0	0	0	0.556	1.543	0.560	1.556
Decalin	$C_{10}H_{18}$	10	0	0	0	0	0.613	1.977	0.603	1.944
n-Tetradecane	$C_{14}H_{30}$	14	0	0	0	0	0.575	1.648	0.570	1.633
1-Heptene	C_7H_{14}	5	2	0	0	0	0.552	1.657	0.555	1.664
1-Pentyne	C_5H_8	3	0	2	0	0	0.529	1.852	0.518	1.813
Toluene	C_7H_8	0	0	0	6	1	0.658	2.961	0.656	2.950
Indene	C_9H_8	0	0	0	8	1	0.676	3.716	0.677	3.725
Propylbenzene	C_9H_{12}	2	0	0	6	1	0.633	2.532	0.638	2.550
Tetralin	$C_{10}H_{12}$	2	0	0	6	2	0.676	2.928	0.685	2.967

The best correlation with experimental measurements was obtained in the calculation of s_c for the 73 fuels; in this case the linear correlation coefficient has an excellent value, being equal to 0.994. The results, as depicted in Figure 2, show ancillary advantages of the employment of s_c as a sooting tendency criterion:

a. The values of s_c (approx. 0.9 to 3.8) cover a wider range than those of φ_c (approx. 0.4 to 0.7), thus making it easier to doscern the differences between various fuels.

b. What is more important, s_c tends to divide the sooting tendencies of the fuels into more rational and intuitively acceptable classes. Thus paraffins have s_c values averaging around 1.5, olefins and alkynes average around 1.8, whereas the average for aromatics is close to 3. Such distinctions are difficult to make with φ_c as the sooting tendency criterion.

The above observations, which show a dependence of sooting tendency on molecular structure similar to that observed for diffusion flames,(3) has led us to attempt a correlation of sooting tendencies in diffusion flames with those in premixed flames. Figure 3 shows a plot of s_c vs. the diffusion flame threshold soot index , TSI(3), for 65 fuels. The linear correlation coefficient has an acceptable value of 0.925, which rises to 0.96 if the four points that are circled in Figure 3 are omitted and the correlation employs 61 fuels. When diffusion flame TSI is compared to φ_c, the correlation coefficient has a much less acceptable value of 0.76, whereas the correlation with ψ_c gives results that are only slightly better (r=0.86).

CONCLUSIONS

1. By employing appropriate weighting factors on the carbon atoms that comprise a fuel molecule, its premixed flame sooting tendency in the form of φ_c can be predicted with acceptable accuracy. The prediction is even better if the sooting tendency criterion is s_c, which assumes incomplete combustion to elemental carbon and water.

2. A linear correlation exists between sooting tendency in premixed flames as expressed by s_c, and sooting tendency in diffusion flames as expressed by TSI.

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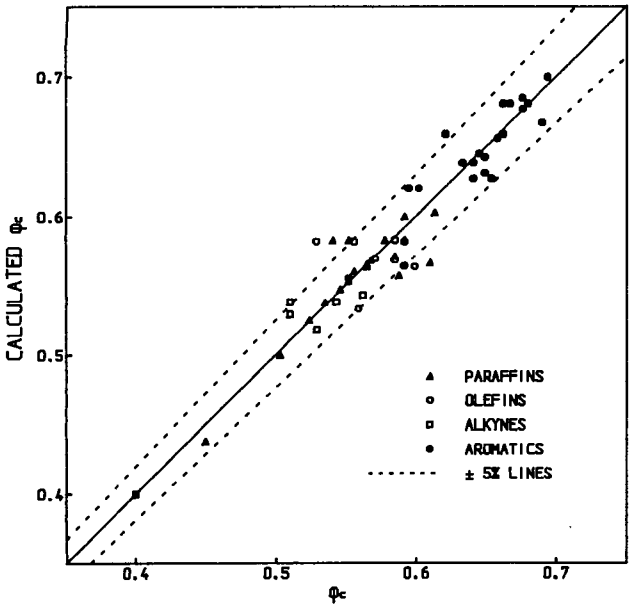

FIGURE 1. CALCULATION RESULTS FOR φ_c

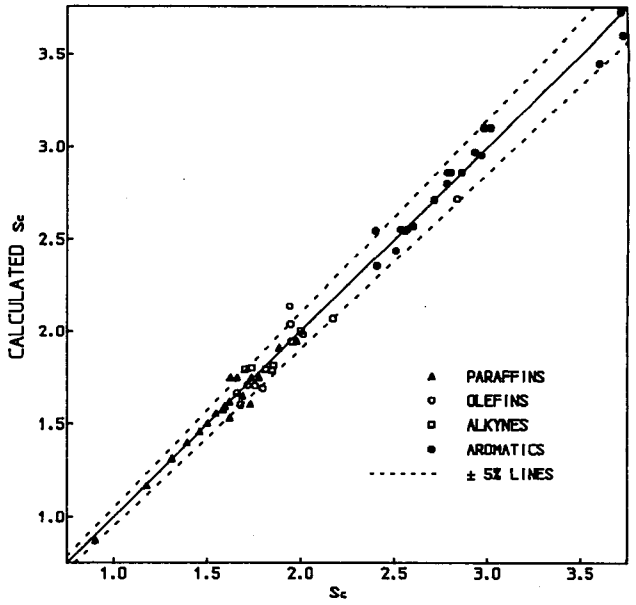

FIGURE 2. CALCULATION RESULTS FOR s_c

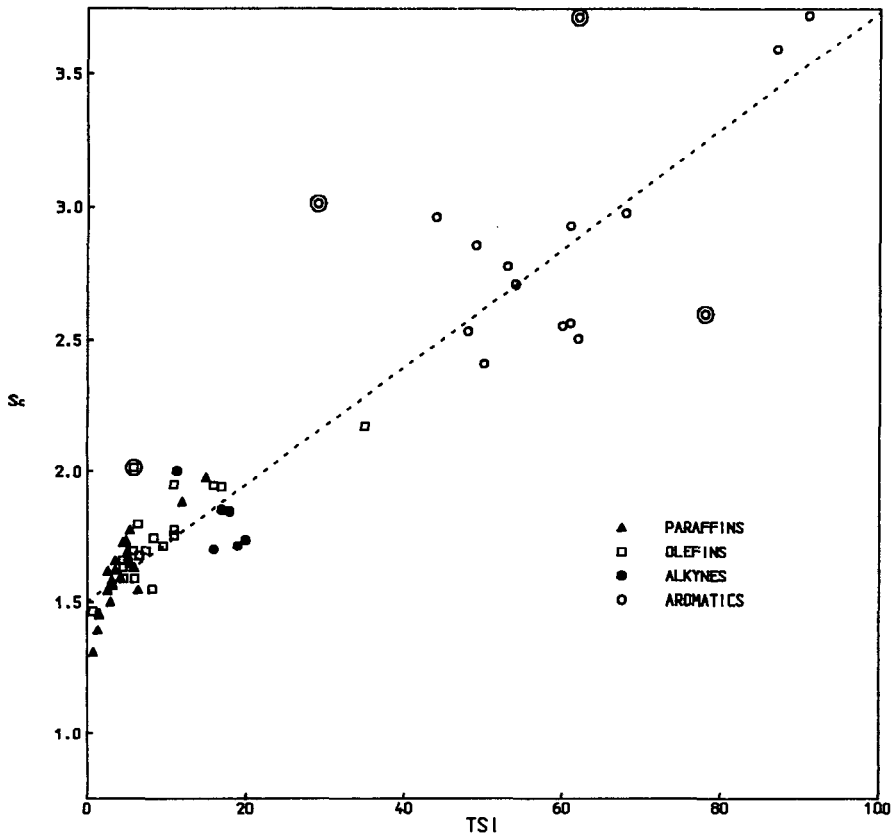

FIGURE 3. CORRELATION OF DIFFUSION FLAME TSI WITH S_c